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Synthesis of β-(trifluoromethyl)furans and spiro-*gem*-dichlorocyclopropanes from cyclic 1,3-dicarbonyl compounds and α-(trihaloethylidene)nitroethanes

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ABSTRACT

While 1,3-dicarbonyl compounds react with (*E*)-1,1,1-trifluoro-3-nitrobut-2-ene in the presence of sodium acetate to produce the target β-(trifluoromethyl)furans, their reaction with (*E*)-1,1,1-trichloro-3-nitrobut-2-ene, under the same conditions, took an entirely different course and gave spiro-*gem*-dichlorocyclopropanes bearing a 1-nitroethyl moiety, with high diastereoselectivity and in good yields.

Conjugated nitroolefins are widely used in organic synthesis due to the high electrophilicity of the double bond.[1] As a result, partially fluorinated nitroalkenes have attracted attention as excellent building blocks for the preparation of various R^F-containing compounds.[2] In particular, polyfluoroalkylated nitroalkenes react with enamines of cycloalkanones and methyl ketones to give β-polyfluoroalkyl-γ-nitroketones,[3] nitro alkylated enamines, and 1,2-oxazine *N*-oxides,[4] as well as 1-pyrroline *N*-oxides.[5] At the same time, very little information is available on the reactions of trihalomethylated conjugated nitroalkenes with 1,3-dicarbonyl compounds. Only one Letter is known reporting the reaction of 3,3,3-trifluoro-1-nitropropene with 1,3-dicarbonyl compounds to give the corresponding addition products.[6] Recently, we reported that 1,1,1-trifluoro-3-nitrobut-2-ene (**1a**) reacted with 1,3-diketones and primary aliphatic amines to give substituted β-(trifluoromethyl)pyrroles via the Grob cyclization.[7]

On the other hand, it is well-known that β-diketones and β-ketoesters add to nitroalkenes to form substituted dihydrofurans or furans depending on the number and nature of the substituents at the nitroalkene double bond.[8] In this furan synthesis, nitroalkenes are commonly employed because the nitro group can act as both a powerful stabilizer of the intermediate anion and as a good leaving group in the aromatization forming a furan ring. In the case of 1,1,1-trifluoro-3-nitrobut-2-ene (**1a**) and 1,1,1-trichloro-3-nitrobut-2-ene (**1b**), it would be reasonable to assume the possibility of an intramolecular Nef reaction occurring with formation of the β-(trihalomethyl)furan core. In this context, and in connection with our interest in the development of CX_3-nitroolefin (X = F, Cl) chemistry,[4,5,7] a method for the preparation of the β-(trihalomethyl)furan system based on the Nef reaction, in a one-pot procedure, attracted our attention. The present communication describes the dramatic effect of the trihalomethyl group on the pathway of the reactions between α-(trihaloethylidene)nitroethanes **1a**,**b** and 1,3-dicarbonyl compounds.

Although a number of methods have been developed for the construction of β-(trifluoromethyl)furans,[9] which are versatile intermediates in synthetic organic chemistry,[10] their simple and convenient synthesis still remains an attractive goal. Furthermore, benzofuran derivatives bearing a trifluoromethyl group at the 3-position have, surprisingly, been poorly investigated, probably due to the few methods available for their preparation.[11]

We found that the reaction of CF_3-nitrobutene **1a** with 1,3-cyclohexanedione, dimedone, or 5-phenyl-1,3-cyclohexanedione resulted in the formation of 2-methyl-3-(trifluoromethyl)dihydrobenzo[*b*]furan-4-ones **2a**–**c**. The procedure is simple and the products were obtained in 41–67% yields, merely by standing a mixture of the reactants and NaOAc (as the base) in ethanol at room temperature for seven days. A plausible pathway leading to the formation of these compounds via intermediates **A** and **B** is outlined in Scheme 1. In a similar manner, reaction with benzoylacetone gave an 83:17 mixture of isomeric furans **2d** and **2′d** in 41% yield. When

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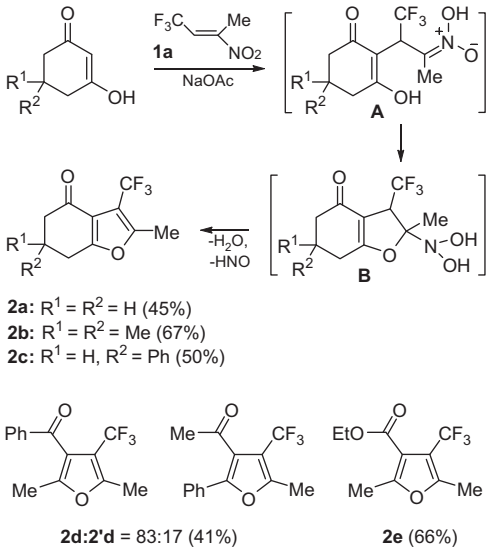
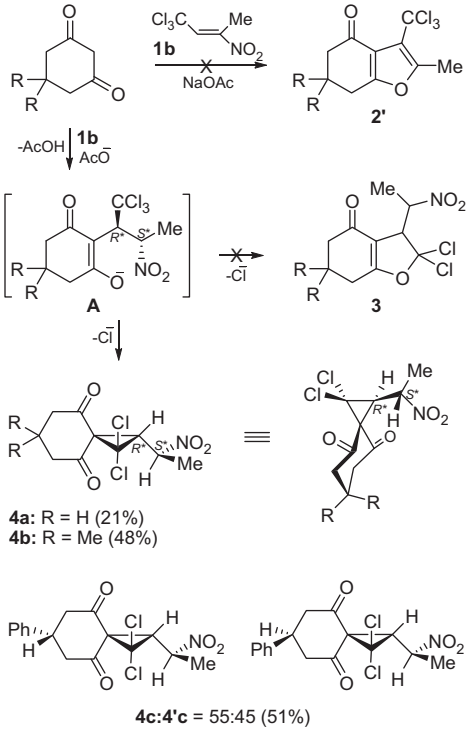


Scheme 1. Reactions of CF_3–nitroalkene **1a** with 1,3-dicarbonyl compounds.

ethyl acetoacetate was allowed to react with nitrobutene **1a**, compound **2e** was obtained in 66% yield as a single regioisomeric product. This approach represents a new synthesis of β-(trifluoromethyl)furans and has advantages with regard to ease of operation and the ready availability of the starting materials. However, Meldrum's acid and its derivatives did not react with 1,1,1-trifluoro-3-nitrobut-2-ene (**1a**) under the same conditions. We believe that this difference arises from the absence of the enolic form of Meldrum's acid in solution.[12] In the ^{19}F NMR spectra of furans **2a**–**e**, the trifluoromethyl group appeared as a quartet at δ 104.4–106.1 ppm ($CDCl_3$, C_6F_6) with $^5J_{F,H}$ = 2.0–2.4 Hz.

Next, and taking into account the above results, it was of interest to evaluate the behavior of 1,1,1-trichloro-3-nitrobut-2-ene (**1b**) in this reaction with cyclic 1,3-dicarbonyl compounds. In this



Scheme 2. Reactions of CCl_3–nitroalkene **1b** with 1,3-cyclohexanediones.

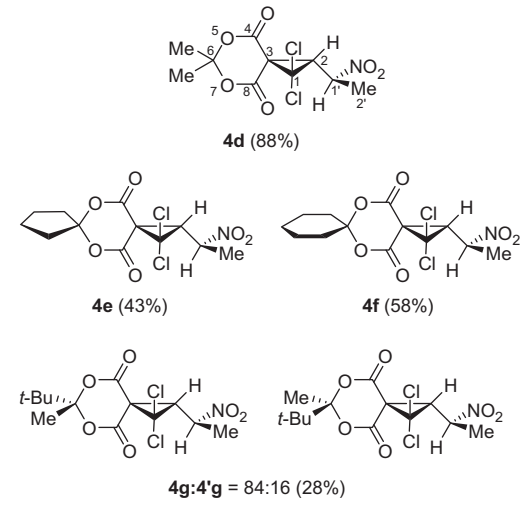


Figure 1. Products **4d**–**g** prepared by cyclopropanation of various Meldrum's acid derivatives.

case, formation of the desired β-(trichloromethyl)furans **2′**, involving the enolic hydroxyl and the *aci*-form, did not occur. As the reactions of the cyclic diketones, such as 1,3-cyclohexanedione and dimedone, with nitroalkenes, having a good leaving group, usually afford tetrahydrocoumaran derivatives,[13] we envisaged that the reaction of **1b** with these 1,3-diketones would produce compounds **3**. However, in contrast to the literature data, there was a marked difference in the propensity toward ring-closure, and interesting results were obtained. Thus, when CCl_3-nitrobutene **1b** was allowed to react with 1,3-cyclohexanedione and dimedone under the conditions described above, the reaction unexpectedly provided spirocyclopropanes **4a**,**b**, which precipitated from the ethanol solution as the sole products, with the stereochemistry as shown, instead of affording the expected tetrahydrocoumarans **3**. A similar reaction with 5-phenyl-1,3-cyclohexanedione gave a mixture of *trans*-**4c** and *cis*-**4′c** isomers (Scheme 2). Their ratio (55:45) was easily determined by ^1H NMR analysis.

In order to determine the scope of this reaction, we tested Meldrum's acid under the same reaction conditions. To our delight, replacement of 1,3-cyclohexanediones with Meldrum's acid and its 2-substituted derivatives resulted in direct and efficient cyclopropanation to give compounds **4d**–**g** in 28–88% yields (Fig. 1).[14] As expected, spirocyclopropane **4g** was obtained as a mixture of two geometric isomers in an 86:14 ratio, which was affected by steric factors. The structures of compounds **4a**–**g** were established by elemental analysis, and IR, ^1H, and ^{13}C NMR spectroscopy. In the ^1H

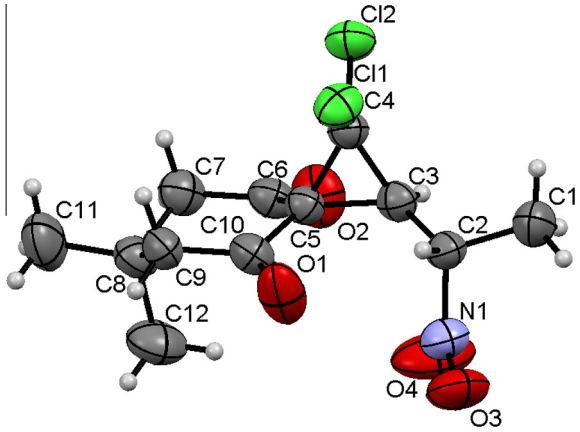


Figure 2. X-ray crystal structure of **4b** (ORTEP drawing, 50% probability level).

NMR spectra, protons H-2 and H-1′ appeared as a doublet and a doublet of quartets at δ 3.30–3.55 and δ 5.25–5.42 ppm, respectively (^3J = 10.5, 7.0 Hz). In addition, to determine the relative configuration of these compounds, single crystal X-ray analysis of **4b**, as a representative example, was performed (Fig. 2).[15] The stereochemistry was assigned unambiguously as (2*R**,1′*S**) and by analogy to the other spirocyclopropane derivatives.

Thus, the reactions of cyclic 1,3-dicarbonyl compounds with CF_3-nitroalkene **1a** produced β-(trifluoromethyl)furans **2**, whereas similar reactions with CCl_3-nitroalkene **1b**, due to the good leaving ability of the chlorine, lead to *gem*-dichlorocyclopropanes **4**, and no furan or dihydrofuran derivatives (e.g., **2′** and **3**). This result is of particular interest because all the important practical methods of synthesizing *gem*-dichlorocyclopropanes consist of the addition of dichlorocarbene to an appropriate alkene.[16]

The simplest explanation for this outcome is a Michael addition followed by cyclization with displacement of chloride from the trichloromethyl group. Such reactions are defined as Michael-initiated ring closure (MIRC) reactions.[17] The first step of the process involves the diastereoselective formation[18] of a new C–C bond in the key intermediate **A** generated via nucleophilic addition with a concomitant [1,3]-H shift, in which the ambident enolate anion can react with the CCl_3 group producing a cyclic compound, which can be either a dihydrofuran **3** or a cyclopropane **4**, as a result of formal [3+2] or [1+2] cycloadditions, respectively. In our case, the cyclization process leads to the stereoselective preparation of spiro-*gem*-dichlorocyclopropanes **4** with a 1-nitroethyl moiety on the cyclopropane ring, and proves that the enolate anion reacts with the CCl_3 group acting as a C-nucleophile (Scheme 2). To our knowledge, cyclopropanation based on the reaction between a trichloromethyl group and an internal C-nucleophile has not been described previously. As dihalocyclopropanes are very useful in organic synthesis[16] this reaction is noteworthy.

A methyl substituent at the α-position of CCl_3-nitrobutene **1b** appears to be a prerequisite for cyclopropane formation and influences the course of the cyclization since the reaction of 3,3,3-trichloro-1-nitropropene gave none of the desired products. It should also be noted that active methylene compounds such as diethyl malonate, ethyl cyanoacetate, acetylacetone, and 1,3-indanedione did not give positive results under the above experimental conditions. This indicates that the presence of the 6-membered ring in the 1,3-dicarbonyl compounds is necessary for nucleophilic attack at the CCl_3 group.

In conclusion, we have shown, for the first time, that the reactions of α-(trihaloethylidene)nitroethanes with 1,3-dicarbonyl compounds affords [3+2] or [1+2] cycloadducts depending on the nature of the trihalomethyl group. In the case of CF_3-nitrobutene **1a**, a new synthesis of β-(trifluoromethyl)furan derivatives was found, while reactions of CCl_3-nitrobutene **1b** proceeded with participation of the trichloromethyl group to give spiro[2.5]octane-4,8-diones. The ready accessibility of the starting materials, good yields, and simple manipulation make the described methods for furan and spirocyclopropane syntheses very useful. Further studies on related reactions are now in progress.

Acknowledgment

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14. *General procedure for the synthesis of compounds **2** and **4**.* To a solution of the corresponding 1,3-dione (1.5 mmol) and NaOAc (0.12 g, 1.5 mmol) in EtOH (7.0 mL) was added CX_3-nitrobutene **1a** or **1b** (1.5 mmol), and the resulting mixture stirred at room temperature for 7 d. The mixture was concentrated under reduced pressure, chromatographed on silica gel (eluting with $CHCl_3$), and the solid formed was recrystallized from CH_2Cl_2/hexane (1:2) to give compounds **2** (colorless needles) or **4** (white powders).
2,6,6-Trimethyl-3-(trifluoromethyl)-6,7-dihydro-1-benzofuran-4(5H)-one (***2b***). Yield 0.25 g (67%), mp 90–91 °C. IR (KBr): 1681, 1628, 1595, 1463, 1363 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (s, 6H, 2Me), 2.39 (s, 2H, CH_2), 2.44 (q, J = 2.3 Hz, 3H, Me), 2.71 (s, 2H, CH_2); ^{19}F NMR (471 MHz, $CDCl_3$) δ 104.5 (q, J = 2.3 Hz, CF_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 12.9, 28.4 (2Me), 34.9, 37.1, 52.4, 109.0 (q, $^2J_{C,F}$ = 38.4 Hz, C-3), 117.5 (C-3a), 122.4 (q, $^1J_{C,F}$ = 267.4 Hz, CF_3), 153.7 (q, $^3J_{C,F}$ = 4.2 Hz, C-2), 165.2 (C-7a), 191.0 (C=O). Anal. Calcd for $C_{12}H_{13}F_3O_2$: C, 58.54; H, 5.32. Found: C, 58.45; H, 5.23.
2-Methyl-6-phenyl-3-(trifluoromethyl)-6,7-dihydro-1-benzofuran-4(5H)-one (***2c***). Yield 0.22 g (50%), mp 85–86 °C. IR (KBr): 1690, 1631, 1593, 1457, 1351 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.47 (q, J = 2.2 Hz, 3H, Me), 2.73–2.83 (m, 2H, CH_2), 3.03 (dd, J = 17.2, 11.0 Hz, 1H, C*H*H), 3.15 (dd, J = 17.2, 5.1 Hz, 1H, CH*H*), 3.55 (m, 1H, CH), 7.23–7.40 (m, 5H, Ph); ^{19}F NMR (471 MHz, $CDCl_3$) δ 104.4 (q, J = 2.2 Hz, CF_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 12.9 (q, $^4J_{C,F}$ = 1.1 Hz, Me), 31.0, 40.8, 45.3, 109.2 (q, $^2J_{C,F}$ = 38.5 Hz, C-3), 118.5 (C-3a), 122.3 (q, $^1J_{C,F}$ = 267.5 Hz, CF_3), 126.7, 127.4, 129.0, 142.0, 153.9 (q, $^3J_{C,F}$ = 4.6 Hz, C-2),

165.3 (C-7a), 190.2 (C=O). Anal. Calcd for $C_{16}H_{13}F_3O_2$: C, 65.31; H, 4.45. Found: C, 65.18; H, 4.58.

(2R)-1,1-Dichloro-6,6-dimethyl-2-[(1′S*)-1′-nitroethyl]spiro[2.5]octane-4,8-dione (**4b**).* Yield 0.22 g (48% in the presence of NaOH), mp 135–136 °C. IR (KBr) 1734, 1705, 1552, 1467, 1445, 1413, 1361 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 3H, Me), 1.25 (s, 3H, Me), 1.84 (d, J = 7.0 Hz, 3H, Me), 2.62 (dd, J = 15.1, 2.3 Hz, 1H, H^e), 2.65 (d, J = 15.1 Hz, 1H, H^a), 2.69 (d, J = 15.1 Hz, 1H, H^a), 2.76 (dd, J = 15.1, 2.3 Hz, 1H, H^e), 3.30 (d, J = 10.5 Hz, 1H, H-2), 5.26 (dq, J = 10.5, 7.0 Hz, 1H, H-1′); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.5, 26.9, 30.1, 30.5, 38.7, 53.8, 53.9, 55.5, 63.3, 77.4, 196.4 (C=O), 199.6 (C=O). Anal. Calcd for $C_{12}H_{15}Cl_2NO_4$: C, 46.77; H, 4.91; N, 4.55. Found: C, 46.70; H, 4.84; N, 4.44.

(2R)-1,1-Dichloro-6,6-dimethyl-2-[(1′S*)-1′-nitroethyl]-5,7-dioxaspiro[2.5]octane-4,8-dione (**4d**).* Yield 0.41 g (88%), mp 190–191 °C. IR (KBr) 1786, 1755, 1553, 1417, 1404, 1387, 1359 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.85 (s, 3H, Me), 1.91 (d, J = 7.1 Hz, 3H, Me), 1.93 (s, 3H, Me), 3.56 (d, J = 10.4 Hz, 1H, H-2), 5.42 (dq, J = 10.4, 7.1 Hz, 1H, H-1′); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.7, 27.67, 27.71, 41.7, 42.0, 64.8, 76.8, 106.4, 160.18 (C=O), 160.21 (C=O). Anal. Calcd for C10H11Cl2NO6: C, 38.48; H, 3.55; N, 4.49. Found: C, 38.49; H, 3.35; N, 4.49.

(2R)-1,1-Dichloro-2-[(1′S*)-1′-nitroethyl]-5,12-dioxadispiro[2.2.5.2]tridecane-4,13-dione (**4f**).* Yield 0.31 g (58%), mp 185–186 °C. IR (KBr): 1784, 1755, 1551, 1451, 1414, 1366 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.49–1.59 (m, 2H, CH_2), 1.76 (quin, J = 6.0 Hz, 2H, CH_2), 1.82 (quin, J = 6.0 Hz, 2H, CH_2), 1.90 (d, J = 7.0 Hz, 3H, Me), 1.99–2.16 (m, 4H, $2CH_2$), 3.55 (d, J = 10.4 Hz, 1H, H-2), 5.42 (dq, J = 10.4, 7.0 Hz, 1H, H-1′); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.6, 21.6, 22.4, 23.8, 36.0, 37.0, 41.7, 42.2, 64.9, 76.8, 107.3, 160.1 (C=O), 160.2 (C=O). Anal. Calcd for $C_{13}H_{15}Cl_2NO_6$: C, 44.34; H, 4.29; N, 3.98. Found: C, 44.43; H, 4.11; N, 3.76.

15. *X-ray diffraction study of compound **4b***. Diffraction data were collected at 295 K on an Xcalibur 3 automatic single-crystal diffractometer (graphite-monochromated MoKα radiation, ω-scan). The structure was solved by direct methods and refined by the full-matrix least-squares method using the SHELX-97 program package.[19] The H atoms were located geometrically using the riding model. *Crystal data for **4b***: $C_{12}H_{15}Cl_2NO_4$, M = 308.15, triclinic crystals, space group P-1, a = 7.6112(9), b = 9.3563(10), c = 10.4839(5) Å, α = 98.561(8), β = 90.887(9), γ = 91.007(9)°, V = 738.03(12) $Å^3$, Z = 2, ρ_{calcd} = 1.387 g/cm^3, μ = 0.448 mm^{-1}, $F(000)$ = 320. Crystallographic data for compound **4b** (CCDC deposition number 934298) have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.
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